

**WHAT IS CLAIMED IS:**

1. A robot autosampler, comprising:
  - a probe carriage being movable between a sample source and an electrospray chip holder and comprising at least one fluid delivery probe which accepts sample from the source and discharges sample to a chip in the chip holder;
  - an electrospray chip holder; and
  - an alignment system which aligns the probe with the chip holder and the chip holder with a detector.
2. The robot autosampler of claim 1, further comprising a voltage probe electrically insulated from and mounted to said fluid delivery probe.
3. The robot autosampler of claim 1, further comprising an electrospray chip mounted to said chip holder.
4. The robot autosampler of claim 3, further comprising a detector in electrospray communication with said electrospray chip.
5. The robot autosampler of claim 4, wherein said detector comprises a mass spectrometer.
6. The robot autosampler of claim 1, wherein said fluid delivery probe comprises a chromatographic column or desalting column.
7. The robot autosampler of claim 1, wherein said fluid delivery probe comprises a capillary tube sample container or larger internal diameter sample container.
8. The robot autosampler of claim 1, wherein said fluid delivery probe comprises a reusable probe, disposable probe, reusable tip, or disposable tip.

9. The robot autosampler of claim 1, wherein said chip holder provides electrospray voltage to the substrate of the chip through the chip mount.
10. The robot autosampler of claim 1, wherein said chip holder provides voltage or ground potential to the substrate of the chip, to at least one nozzle to provide or control electrospray.
11. The robot autosampler of claim 1, wherein said fluid delivery probe provides electrospray voltage to the fluid.
12. The robot autosampler of claim 2, wherein said voltage probe provides electrospray voltage to the surface of the chip, independently to individual nozzles, groups of nozzles, or all nozzles at once.
13. The robot autosampler of claim 3, wherein said electrospray chip further comprises a plurality of individual conducting pads applied on the back of the chip to apply voltage.
14. The robot autosampler of claim 3, wherein said electrospray chip further comprises metal coatings applied on the front of the chip to apply voltage.
15. The robot autosampler of claim 1, wherein said fluid delivery probe further comprises a seal which prevents leakage during delivery of the fluid to the chip.
16. The robot autosampler of claim 3, wherein said electrospray chip comprises a plurality of electrospray devices, each generating one or a multiple of electrospray plumes when activated.
17. The robot autosampler of claim 3, wherein said electrospray chip comprises multiple electrospray devices grouped in a high-density array, each generating one or a multiple of electrospray plumes when activated.

18. The robot autosampler of claim 1, further comprising an assembler control unit in communication with the autosampler.

19. A method for automated manipulation of multiple samples for generation of multiple electrosprays in communication with a detector, comprising:

providing a robot autosampler, which can be programmed to engage a tip onto a fluid delivery probe, load the tip with sample containing at least one electrolyte, transfer the sample loaded tip to communicate with an electrospray chip containing at least one electrospray device, electrospray the at least one analyte, discard the used tip, and engage another tip onto the probe to repeat the loading, transferring, and electrospraying cycle;

engaging a tip onto the autosampler probe;

loading the probe tip with a sample containing at least one analyte;

transferring the at least one analyte to at least one electrospray device on the electrospray chip;

electrospraying the at least one analyte from at least one electrospray device on the electrospray chip;

manipulating the electrospray chip in communication with a detector in a manner to detect analyte from the electrospray, and

repeating the engaging, loading, transferring, and electrospraying cycle.

20. The method of claim 19, wherein said detector is a mass spectrometer.

21. The method of claim 19, wherein said tip is pre-loaded with a sample containing at least one analyte.

22. The method of claim 19, wherein said tip is reused.

23. The method of claim 19, wherein control voltages are applied to the electrospray device by the autosampler.

24. The method of claim 19, wherein said automated manipulation is controlled by programmable computer software.